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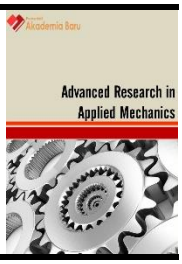


# Effect of Thermal Soak Time Towards Polyimide Based-Carbon Tubular Membrane

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**ABSTRACT**

Tubular carbon membrane (TCM) was prepared form BTDA-TDI/MDI (P-84) polyimide (PI) has a main precursor that combines with nanocrystalline cellulose (NCC) through controlled carbonization condition. Consideration of the thermal soaking time through the heating process is needed to maintain the proficiency of resultant TCM's. Thermal soaking time of 30 minutes, 60 minutes, 90 minutes, and 120 minutes was investigated to study the gas properties of the final TCM's. In the course of TCM's separation, single gas permeation experiments of $CO_2$ and $N_2$ are performed to investigate the transport mechanism. The PI / NCC TCM's developed at 120 min of thermal soak time from this study showed the most impressive $CO_2/N_2$ performance, selectivity of 66.32±2.18 respectively.

***Keywords:***
Tubular Carbon membrane, Thermal soaking time, BTDA-TDI/MDI (P-84) polyimide, Carbon dioxide separation

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## 1. Introduction

Several researchers have recently improved the concept by combining new precursors and controlling the production of membranes to generate high performance membranes. The market for membrane with favorable chemical properties and, most significantly, enhanced separation efficiency encourages an emerging technology in membrane gas separation. Separation processes of membranes are not a new invention and have developed rapidly over decades [1,2]. Polymer membranes, typically in the form of flat sheets or hollow fibres, are able to achieve reasonable permeability and selectivity at a lower price and through simpler production processes [3]. Although these membranes seem to be involve to the gas separation industries, constraints including the efficiency trade-off known as the Robeson upper-bound correlation were one of the actual reasons for its low marketing growing [4,5]. A few researchers have shown strong interest in the TCM processing studies due to the lack of polymeric membrane performance [6]. Essentially, TCM has a

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high volume of pores with high separation factors, known as high thermal and chemical resistances [7,8].

Among all these varieties of membranes, TCM are historically among the most suitable candidates for gas separation due to their easy preparation routes, the multitude of precursor availability [9, 10]. The ability to develop the final structure's properties and also the high level of scientific expertise on the subject. Thermal decomposition of polymer precursors produces pure carbon materials; called TCM. Because of its highly aromatic composition, these materials can withstand high temperature with a disordered sp2 hybridized carbon sheet and angle of disorientation. In addition, the researchers found that TCM produced high permeability and selectivity without losing functionality compare from those commonly found with polymer membranes [11]. This is because of the definite and disordered structures of carbon material are differing from zeolites. In gas separation applications, carbon materials provide perfect pore size dispersal that offers homogeneous defect-free membranes. While substantial work has been recorded since the advent of TCM, the need to improve these membranes gas separation properties matters greatly if they want to become feasible for practical applications [12]. Nonetheless, during carbonization, the structure of membrane and permeation of gas are affected by carbonization conditions. For this reason, so far as TCM's are involved, the great accomplishments of researchers working in this area is the study on thermal soak time.

The factors that affecting membrane transport properties are the phases of carbonization at final temperature of thermal soaking time (30,60,90, and 120 minutes). Previous research by Lua and Su developed Kapton® polyimide TCM by controlling carbonization temperature, rate of heating and carbonization atmosphere [13]. Other study proved that conditions of carbonisation have noticeable effects on TCM gas permeation properties [9]. Thermal soaking time helps to monitor the level of volatile polymer membrane components during the carbonization process [14]. Nevertheless, it is suggested that small pores of TCM's can be obtained using the highest thermal soak rate [15]. Furthermore, the highest thermal soaking period will decide the rate of evolution of volatile precursor components during the process of heat treating [16]. Some changes are observed as thermal soak time increases, changes in morphology to a more compact structure, narrower pore width, lower total pore density, finer pore size distribution, and smaller pores. Throughout this analysis, performance of gas permeation will also be affected by the relations among properties of membrane and thermal soaking period.

Comprehensive focus was given for developing the TCM with a large selection of gas separation precursors and the work was focuses on the effect of heat treatment on the soaking time [17]. Because of the capability of polymers to endure high temperatures through the process of carbonization, PI-copolyimide was treated as the principal precursor [18, 19]. This material exhibits outstanding gas selectivity, which for polymer membranes is one of the most noteworthy ever reported [20, 21]. Our research group has recently recycled newspapers to synthesize nanocrystalline cellulose (NCC) [9]. Thanks to their biodegradability, NCC research in the nanotechnology industry has grown significantly. Our primary concern in NCC is its rod-like nanostructure and low decomposition temperature. Compared to the microstructure additive, the NCC nanostructure might breakable within the polymer of chain. Some scientific research related to thermal soak time during heating process is however incomplete, based on the previously reported analysis. Therefore, this work will focus primarily on preparing and characterizing PI / NCC polymer blends with manipulation of thermal soak period. In this analysis, the performance of gas separation will be performed to analyse the relation between the pore structure and the performance of gas separation.

## 2. Heat Treatment

### *2.1 Materials*

The performances of carbonized membranes are affected by structure of molecular polymer precursor. Polyimide is one of the precursors of polymers due to its superior penetrating diffusive and strong molecular sieving features. Pellet-shaped polyimide (PI) (P84, Merck) was used as the primary membrane formation material. N-methyl-2-pyrrolidone (NMP, Sigma Aldrich) was used as a substrate to dissolve polymer without purification. At present, nanocrystalline cellulose (NCC) is not available on the market and was previously prepared in this study [22]. Shanghai Gongtao Ceramics Ltd. supplied commercial tubular ceramic (nominal 1kD cut-off, outer diameter: 13 mm, inner diameter: 11 mm, porosity: 40-50 percent, average pore size: 0.2 µm). $TiO_2$ (Average particle size: 4.5-5.5 mm, is used to support the membrane support with a length of 8 cm and Zinc oxide ($ZrO_2$) (Average particle size: 2-3 nm) was layered on the inner surface.

### *2.2 Preparation of TCM's*

TCM was designed using solution of dope consisting of 15wt percent BTDA-TDI / MDI (P84), which dissipated as a solution in NMP after drying in an oven at 50°C for a day. The dope solvent then will be sonicated to eliminate trapped bubbles from the solution. NCC was added to the mixture slowly and stirred continuously until homogenous solution were obtained. At 600 rpm, the solution was then automatically swirled until all polymer pellets had been dissolved completely. The solution of dope was then will go through sonication process before the dip-coating process to eliminate every air bubble confined in the solution. For 15 minutes, the ceramic tube reinforcement was submerged in the solution of dope followed by drying for a day in a room temperature. The dip-coating process was repeated twice to remove pinholes in the structure of the membrane. The prepared polymeric membrane was then made to undergo aging at 80 °C for a day, immersed into methanol for 2 hours and let it dry for 24 hours in a room temperature. This process repeated twice before heat treating process. The polymer membranes were subsequently put in a carbolite wire wound tube furnace (Model: CTF 12/65/550) for heat treatment. The length of the furnace tube is about 75 cm with heating zone of 60 cm and the diameter is about 12 cm. At stabilization temperature of 300°C and final carbonization temperature at 800°C, heat treatment process was performed. At the other side, the samples were measured under air flow at 30, 60, 90, and 120 minute's thermal soaking times. The prepared membranes were allowed to cool down at room temperature as each heating process was performed.

### *2.3 Pure Gas Permeation Measurement*

Membrane quality can be categorized into two significant parameters which are selectivity and permeance. The membrane of carbon was tested using a method of internal gas permeation. The system is made up of flexible hose, permeation cell, valve, pressure regulator and soap bubble meter. Stainless steel with a module length of 14 cm, the 8 cm carbon tubular membrane was mounted inside the stainless steel tubular frame. In order to prevent leakage, the membrane was installed with rubber O-rings during the test. Two different gases, namely $N_2$ and $CO_2$ were fed separately into the module at a transmembrane pressure of 8 bars. The membrane's permeance and selectivity were determined using the equations stated as below:

Permeance, *P:*

$$(P/l)_i = \frac{Q_i}{\Delta p.A} = \frac{Q}{\eta \pi D l \Delta P} \quad (1)$$

Selectivity, α:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B} \quad (2)$$

where P/l is the membrane permeance, Qi is the gas i volumetric flow rate at standard temperature and pressure ($cm^3$ (STP/s), p is the difference of pressure between feed and permeation sides of membrane (cmHg), A is the surface area of membrane ($cm^2$), n is the fibers quantity in the module, D is the membrane outer diameter (cm), and l is the effective membrane length (cm). Definition of selectivity can be described as the permeation ratio of fast gas permeation to slow gas permeation.

## 3. Results and Discussion

It was reported that controlling thermal soak time provided the high selectivity TCM. The gas permeance of two pure gases of molecular with different sizes $CO_2$ (3.30) and $N_2$ (3.64) were measured at a feed pressure of 8 bars through the resulting TCM's formed from various carbonization conditions.

### *3.1 Effect of thermal soak-time on gas permeation properties*

Consequently, in understanding the efficiency of TCM gas separation, one factor depends on the thermal soaking time through the heating process. Favvas and co-workers researched the effect of carbonization variables on P84-based TCM transport properties [18]. The experimental results indicated that as the thermal soak time increased, the membrane's pore structure was slightly affected, leading to increased gas selectivity [19]. Other studies related to thermal soak time modification are by Foley and co-workers. By increasing thermal soak time, the micropore size in the TCM was decreased. In fact, the porous structure will start to move closer to the graphite and nonporous structure; resulting increasing in selectivity results.

Table 1 shows gas separation performance of TCM's produced from different thermal soak time. Unfortunately, some structural vestiges of the original precursor are still preserved when heat treatment processes were uncompleted, and this had been supported by Mariwala and Foley [23]. Therefore, an optimum duration for thermal soak time is needed to remove completely the noncarbon elements.

**Table 1**
Gas separation performance of TCM's produced from different thermal soak time

| Samples | Permeance (GPU) | | Selectivity |
|---|---|---|---|
| | $CO_2$ | $N_2$ | $CO_2/N_2$ |
| **CM-30minutes** | 68.11±2.72 | 2.2±1.46 | 30.96±1.88 |
| **CM-60minutes** | 107.46±1.82 | 2.6±3.11 | 41.33±2.67 |
| **CM-90minutes** | 158.92±2.26 | 2.9±3.21 | 54.08±3.12 |
| **CM-120minutes** | 198.21±1.56 | 3.0±1.37 | 66.32±2.18 |

The factors of carrying out TCM with higher thermal soaking time is to allow pores to shrink, resulting in superior selectivity results. In addition, by using 120min thermal soak time, carbon structure will be generated to be packed more orderly at high carbonization temperature with smaller micropores. A prolonged thermal soaking time has been reported to create high selective membrane [16].

## 4. Conclusions

Tubular carbon membrane (TCM) was successfully prepared form BTDA-TDI/MDI (P-84) polyimide (PI) and nanocrystalline cellulose (NCC) over controlled carbonization condition. The thermal soaking time of 30 minutes, 60 minutes, 90 minutes, and 120 minutes was effectively explored in this study. The PI / NCC TCM's carbonized at 120 min of thermal soak time exhibited the maximum reading for $CO_2/N_2$ performance as well as the highest selectivity of 66.32±2.18 respectively.

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